ION-HEAT MODIFICATION OF INORGANIC DIELECTRICS PROPERTIES

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The influence of an ions irradiation and subsequent annealing in vacuum on mechanical and electrophysical properties of ir ganic dielectrics examined. The opportunity of purposeful regulation of their surface resistivity in limits $10^{13}...10^{3}$ Ohm per squ (Ω/□) is shown. The modes of modification ensuring deriving on a surface of dielectrics a thermostable resistive coatings are give

Introduction

The irradiation of a solid state by ions calls in a near-surface layer complex of changes affecting nuclear and electronic subsystems. Atoms displacement and pulverization are result of elastic interaction of ions with lattice atoms. As against metals in dielectrics the role of inelastic interactions accompanying with atoms ionization and electronic subsystem excitation is important. The concentration of electronic excitations will increase with diminution of ions mass and with magnification of their energy. Result of elastic and inelastic interaction is the formation in near-surface layer of new disequilibrium state distinguished on structure and properties from initial. Postimplantation annealing, stimulating in near-surface layer the complex physico-chemical and structural - phase changes, calls further transformation of dielectrics properties and fixes the reached changes.

After ion-heat modification the near-surface layer of inorganic dielectrics represents "composition" containing at the same time with defects and implanted elements unregulated distribution of conductive and - or semiconductive particles having different size and shape [1]. The majority of particles is separated by dielectric layers with high concentration of defects and thickness $1.0...10^4$ nm. There are also chains of contacting among themselves particles. The marked building elements and inhomogeneities differently influence on materials properties.

In this work the brief analysis of literary dates including mechanical properties change of dielectrics irradiated with continuous ions bunches by a current density 1...10 $\mu A/cm^2$ is adduced. The authors investigations of ion-heat modification of electrophysical properties of materials are given. In both cases the single crystals of oxides and alkali-halide compounds, oxide and nitride ceramics of different composition utilised. The irradiation of materials for investigation of electrophysical properties was fulfilled in a pulse-frequency mode by ions at energy 50...150 keV, the current density in impulse made $10^{-2}...10^{-3}$ A/cm^2, the fluence varied in limits $\Phi=10^{13}...10^{17}$ cm^{-2}. The post-implantation annealing was carried out in vacuum at residual pressure P<1 Pa and T_{an}=300...2000 K.

I. Mechanical properties change

The ions implantation influences on strengthening properties of near-surface layer and last effects on the properties of volume. Microhardness [2-7] and stability to crack formation at local loading [2-4,6,8] and strength of adhesion of dielectrics are raise [9,1 Coefficient of friction and the wear rate redu [2,3,11,12]. The flexural strength is incremented 10...30% on the average [3,6,8,13]. Changes of sin crystals are more significant, than of polycrystals a glasses [3,13-16]. The quantitative changes of prop ties are defined by conditions of irradiation and subs quent thermal treatment, are stipulated by induc defects generation, their annealing and transformat into complexes, and structural changes, formation solid solutions and new phases. The contribution strengthening from dispersion mechanism, solid sc tion formation and grain – boundaries participation h determining value for doped by ion implantation ne surface layer. Deformation strengthening is determir by dislocation structure of underlying layer. The doı nant mechanism of strengthening depends on cheı cal nature of the introduced atoms too. The no gases ions are applied expediently to modification mechanical properties after preliminary depositior metal film on dielectric (film thickness does not exce depth of ions run) [5,17].

II. Modification of electrophysical properties

The electrophysical properties of dielectrics surfa are sensitive to radiative and subsequent thermal ac

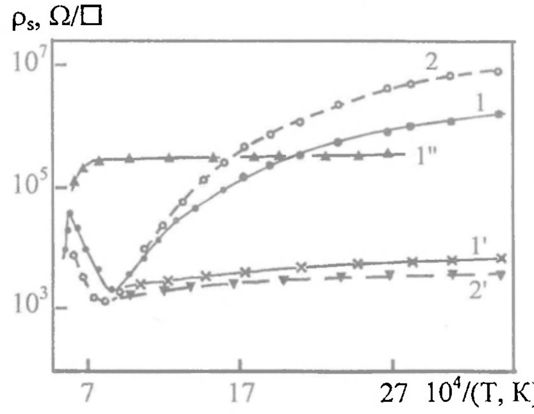

Fig. 1. Surface resistivity of implanted (1, 2) and annealed 1'', 2') ceramics on a basis Al_2O_3: 1, 1', 1''-BK94-2, 1'- aft annealing at 1100 K, 1''- after annealing at 1650 K; 2, 2' BK94-1, 2'- after annealing at 1100 K. A fluence of carbc ions 10^{17} cm^{-2}.

tions also. The ions irradiation reduces surface res tivity ρ_s on 4...8 orders of magnitude (fig. 1). Reesta lishment of irradiated surface up to metal realize compounds easily losing the anions at ion bombardment (for example, alkali-halides). The enrichment of near-surface layer by component having high pressure of vapours above than some concentration can lead to it spontaneous desorption both at irradiation, and at the subsequent heat treatment in vacuum. Result of desorption is the drop of electrical conduction σ (fig. 2).

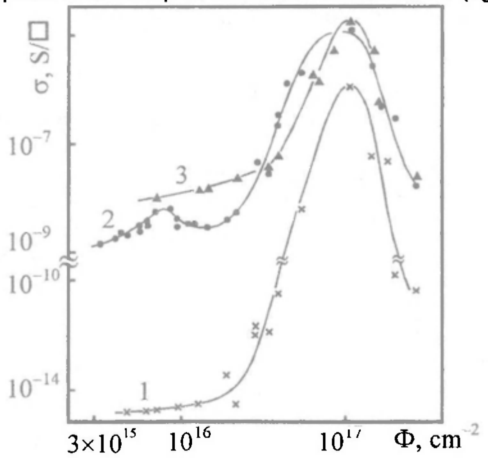

Fig. 2. Effect of carbon ions fluence on an electrical conduction KBr at temperature 290 (1), 650 (2), 720 K (3).

The postimplantation heat treatment promotes the further drop ρ_s (fig. 1). Stabilization $\rho_s(T)$ of heat-resistant materials occurs after annealing at 950...1500 K. Result of ion-heat modification is forming on surface a thermostable conductive coating. Surface resistivity can be governed by treatment modes in limits $10^3...10^{15}$ Ω/□. The temperature coefficient of ρ_s does not exceed $10^{-4}...10^{-3}$ K^{-1} in temperature interval up to 1500 K. An optimum range of annealing is individual for each material and makes

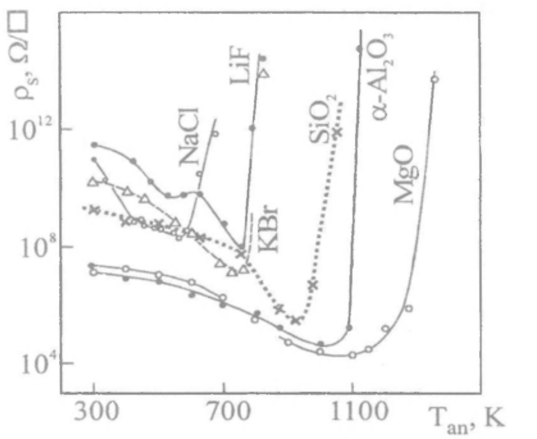

Fig. 3. Postimplantation annealing temperature effect on change of surface resistivity at T=300 K of single crystals and quartz glass irradiated $\Phi=10^{17}$ C^+/cm^2.

550 ... 750 K for alkali-halide crystals, 950...1200 K for oxide ceramics (fig. 3) and 1100...1500 K for nitride ceramics (fig. 4). Medium of annealing are vacuum or noble gases. This excludes an electronic exchange between the modified surface and active gas phase reagents calling restoration of properties owing to electonic-ionic reations between defects.

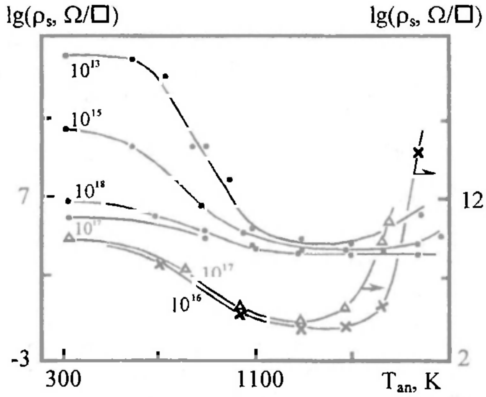

Fig. 4. Postimplantation annealing temperature effect on change of surface resistivity at T=300 K irradiated nitride ceramics. Numerals at curves ingicates fluence of carbon ions, cm^{-2}: ●- boron nitride; Δ- silicon nitride; × - aluminium nitride.

The ions of light element and ions of elements, capable to substitute lattice atoms and to form semiconductive solid solutions, increment conduction on 10...12 orders of magnitude. Action of heavy ions is less effectively.

The greatest change of dielectric properties is observed at ions fluence $10^{15}...10^{17}$ cm^{-2} in materials having high portion of covalent component in interatomic bond (nitride ceramics, fig. 4). Mode of ionic intermixing allowing owing to introduction of recoil atoms and radiation-enhanced diffusion to increase additionally concentration of impurity elements in modified layer is effectively too. Essential changes of conduction of multicomponent oxides systems (where ionic component of chemical bond dominates) are observed only in materials with low contents of SiO_2 both as glasses phase in intercrystallite boundaries and as basic crystalline phase. The conductive coating formed on surface of nitride ceramic materials is more thermostable than a similar coating on oxide ceramic.

The coating on polycrystals is more stable against high temperature effect, than analogous coating on single crystals and glasses (compare fig. 3 and 4). It is stipulated by presence in polycrystals high concentration of boundaries. Boundaries and near-boundary regions of crystallites, having distorted electronic structure and uncompensated charge, determine a spatial distribution, sink and fixing component of Frenkel pairs at irradiation, and degree of transformation defects clusters and diffusion of impurity at heating too. Segregation of new phases at annealing are fixed at first on boundaries, and at higher temperatures in crystallites also. The stability of formed compounds in polycrystalline materials is higher, than in single crystals. Such situation is exhibited especially explicitly on nitride ceramics having a composite hierarchy structure with the fragments size 50...100 nm. Heat stability of any modified materials properties raises, if implanted elements are formed with matrix a stable covalent bonds.

Influence of chemical interaction between introduced elements and matrix atoms at postimplantation annealing observed on example of polycrystalline corundum irradiated by ions Cu^{+n} and Ti^{+n}, having fraction substitutional cations of lattice Al_2O_3 accordingly 0.05 and 0.9 [18]. The modified materials differ not only behaviour ρ_s (T_{an}) and thermal stability, but also mechanism of conduction. Positive sign of temperature coefficient of conduction (diminution σ with T growth up to 800...900 K) is characteristic only for polycrystalline corundum irradiated by Ti^{+n} ions and annealed in vacuum at 1400...1700 K. The investigations of electronic structure and chemical reactions have shown, that for system $Ti\text{-}Al_2O_3$ characteristicly strong chemical interaction of titanium with oxygen and aluminium, and for system $Cu\text{-}Al_2O_3$ only with oxygen [19].

In alkali-halide crystals the most essential properties changes are called by ionic intermixing mode (fig. 5). Their conduction at 300 K by modes of ion-heat

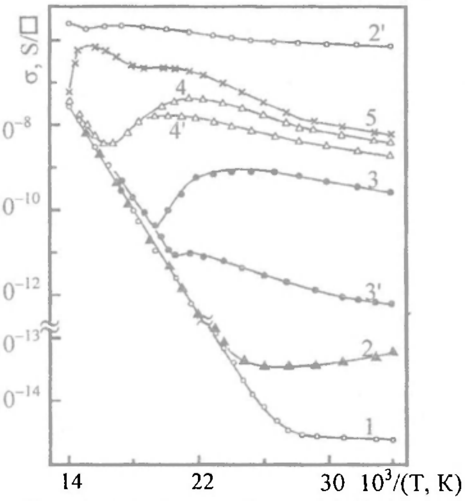

Fig. 5. Electrical conduction of crystals LiF after ions implantation (1-5), postimplantation heat treatment at 500 K (3′, 4′) and modification in ionic intermixing mode (2′). A fluence of carbon ions, cm^{-2}: 1– 1.6×10^{16}; 2, 2′– 3.8×10^{16}; 3, 3′– 5.5×10^{16}; 4, 4′– 7.7×10^{16}; 5– 1.4×10^{17}.

modification can is enlarged up to 10^{5} ... 10^{-6} Siemens per square (S/□) (fig. 3, 5). Conductive near-surface layer has both positive, and negative temperature coefficient of conduction. The conduction growth is stipulated by transformation of the induced defects in impurity-vacancy complexes. Diminution σ is result of changes of concentration and morphology of metal formations (these formation are formed in volume and on a surface of modified layer) and their removal from surface at T=530...600 K. Annealing of defects at T>700 K also reduces σ. The enrichment of modified layer by metal realizes owing to selective pulverization of material at irradiation and diffusion of F-centres to surface at heating. Coatings on alkali-halide crystals surface having stability in time conduction $\sigma>10^{-8}$ S/□ at T>380 K are forms at modification only in ionic intermixing mode (fig. 5). The activation energy charge carriers in such layers makes 0.2...0.5 eV.

Ions implantation in ceramics beforehand heat up to T_i>500 K and subsequent annealing do not all to create a modified layer with $\sigma>10^{-8}$ S/□. Stal against temperature action properties are formed af annealing at 900...1200 K (T_i<1000 K) and/or 1700...1750 K (T_i>500 K). Conduction of n-type dor nates in layers having $\sigma>10^{-9}$ S/□, however shift Fermi level to conduction band is expressed to lesser degree, than in case of strong magnification conduction (T_i<500 K, $\sigma\geq10^{-4}$ S/□). The conduction p-type is characteristic for a weak-conductive surfa having $\sigma\leq10^{-11}$ S/□. The behaviour ρ_s(T) is determin by a stability to T_i of generated point defects and th simple complexes. The defects, induced at hic temperature implantation, are much more stable, th defects proper low-temperature implantation.

Conclusion

The ion-heat action modifies surface properties inorganic dielectrics. Semiconductive coating form by modification is thermal stable and can be utilised the practical purposes at temperature up to 1800 K.

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